

Quick-Starting Fuel Processors

2003 Hydrogen and Fuel Cells Merit Review Meeting

May 19-22, 2003, Berkeley, CA

Objective

- ❖ Study feasibility of fast-starting a fuel processor
 - To meet DOE targets for on-board fuel processing
 - 60 seconds (2005); 30 seconds (2010) from 20°C

Relevance : On-board fuel processing will ease the transition to the hydrogen economy

Addresses Technical Barriers

I: FP Startup, Transient Operation

L: CO Clean-up

M: FP Efficiency

Feasibility of Acceptable Start-Time Experimental Reformer

Argonne Electrochemical Technology Program

Reviewer Comments

- ❖ Demonstrate a fast-start strategy
- ❖ Focus on a specific design
- ❖ Solicit guidance from industry on practicality of design changes

- ✓ A fast-start strategy has been developed
- ✓ A specific design which can implement the strategy has been defined
 - Industrial partners interested in outcome of specific design are providing input
- ✓ The strategy will be tested in Oct.'03 - Jan.'04

Program Approach

- ❖ Consortium of DOE laboratories, universities, and private enterprise
 - National Labs contribute core technologies
 - Private industry contributes components, expertise
 - University resources provide support
 - Faculty members contribute expertise
 - Students participate in experimental activity
 - Information exchange through multiparty NDA
- Project Duration: October 2002 – June 2004

Technical Approach

- ❖ Design a “ATR/Shift/PrOx” fuel processor
 - Capable of implementing a start-up strategy
 - Consistent with application-specific constraints
 - e.g. efficiency, etc.
- ❖ Set up in the laboratory as a learning tool
 - Build and test experimental hardware, apparatus
 - Analyticals, balance-of-plant, PC-based data acq./control
- ❖ Supported by modeling and small experiments
 - GCTool, CFD
 - Experiments to confirm expectations
 - e.g., ignition of liquid gasoline in the ATR at start-up

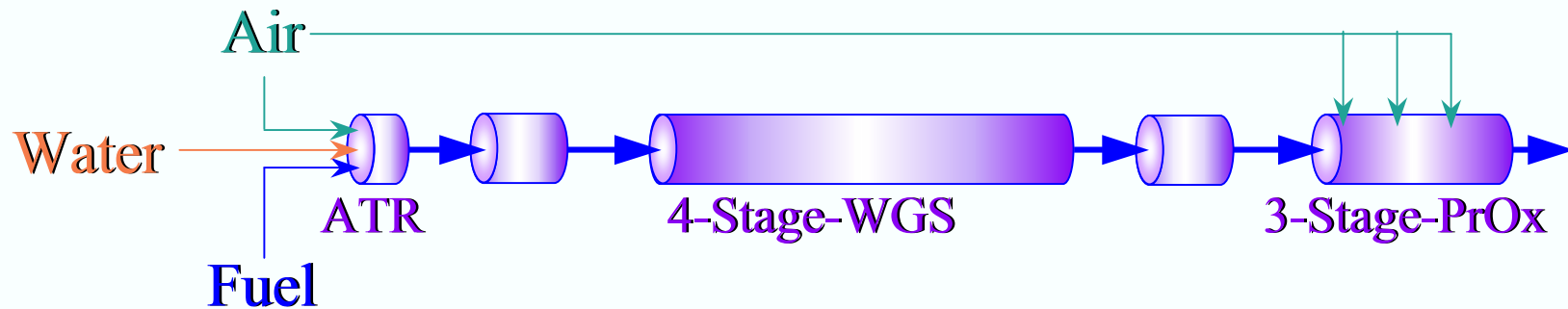
Demonstrate fuel processor generating reformat gas at 90% capacity (9 kWe)

❖ Start-up Time	60 seconds
❖ FP Max. Capacity	10 kWe
❖ Start-up Capacity	9 kWe (145 SLPM of H ₂)
❖ Fuel	Gasoline
❖ Reformate @ 61 sec.	H ₂ > 30%; CO < 50 ppm
❖ Demonstration	Jan. 2004

Project Milestones

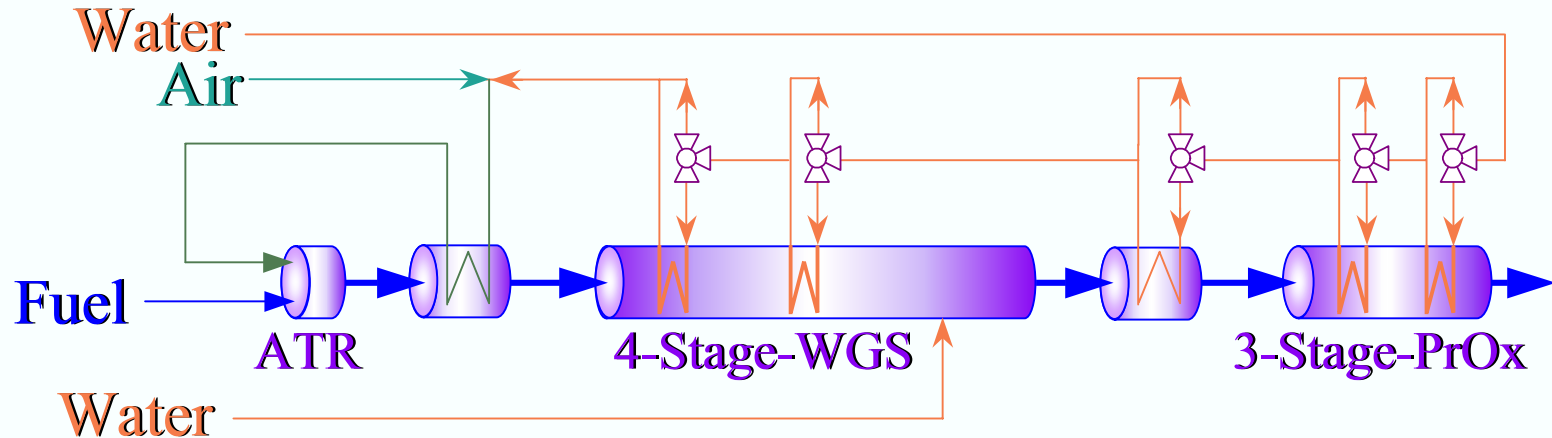
<i>Milestone</i>	<i>Date</i>	
FP Defined	Dec. '02	✓
FP Component Sizes Specified	Mar. '03	✓
Components Received at ANL	Jun. '03	
FP System Assembled	Aug. '03	
FP Tests Begin	Oct. '03	
Demonstrate Performance	Jan. '04	
Conclusions to DOE	May '04	

Fuel processor is based on ATR, followed by WGS and PrOx



- ❖ 4-stage water gas shift reactor
- ❖ 3-stage preferential oxidation reactor
- ❖ Thermally integrated unit

Temperature control features prominently in system definition



- ❖ Heat removal in WGS and PrOx units are on-demand only
- ❖ Liquid water injected before WG4
 - Heat exchanger not meaningful at low heat duty
 - Higher $[H_2O]$ favors shift reaction

O/C, S/C, and $T_{Approach}$ significantly impact the design

❖ Higher O/C

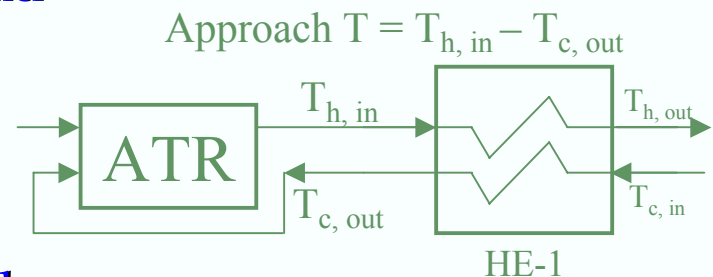
- Raises ATR temperature
 - Reduces CH_4 slip, improves $\text{H}_2 + \text{CO}$ yield
 - Increases CO/CO_2 ratio, increases WGS load
 - Increases heat loads on HEx (more shift rxn, mass flows)
 - Material durability (catalyst, housing, post-ATR HEx)
- May reduce H_2 concentration in reformat
- May reduce H_2 yields, lowering FP efficiency

❖ Higher S/C

- Lowers ATR temperature
- Lowers CO/CO_2 ratio, reduces WGS load
- Shrinks WGS size significantly
- Reduces fuel processor efficiency

❖ Higher approach temperature in HEx-1

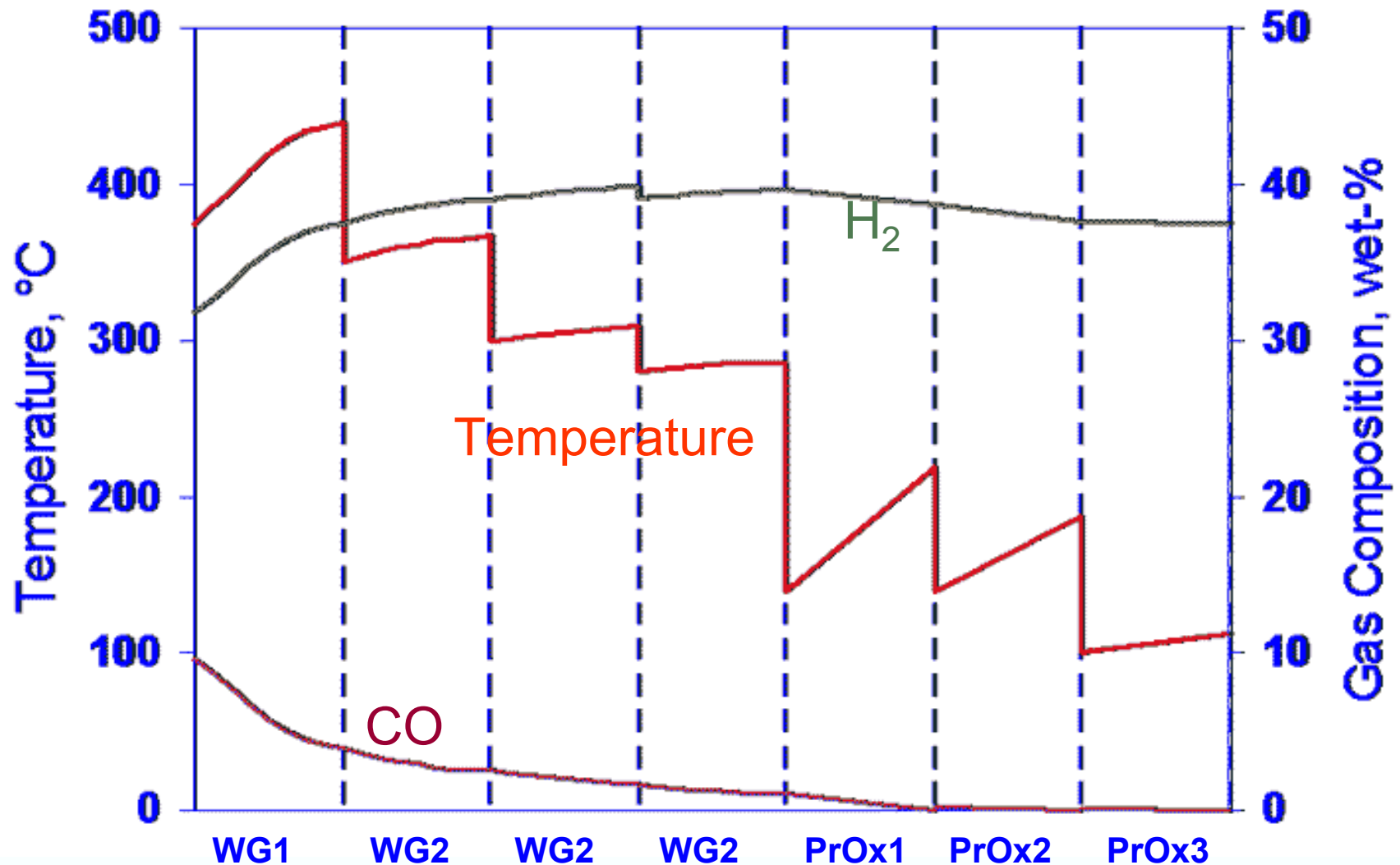
- Smaller and lighter heat exchanger
- Increases (slightly) heat load of heat exchangers
- Requires more O/C to achieve desired ATR temperature
- Permits higher S/C



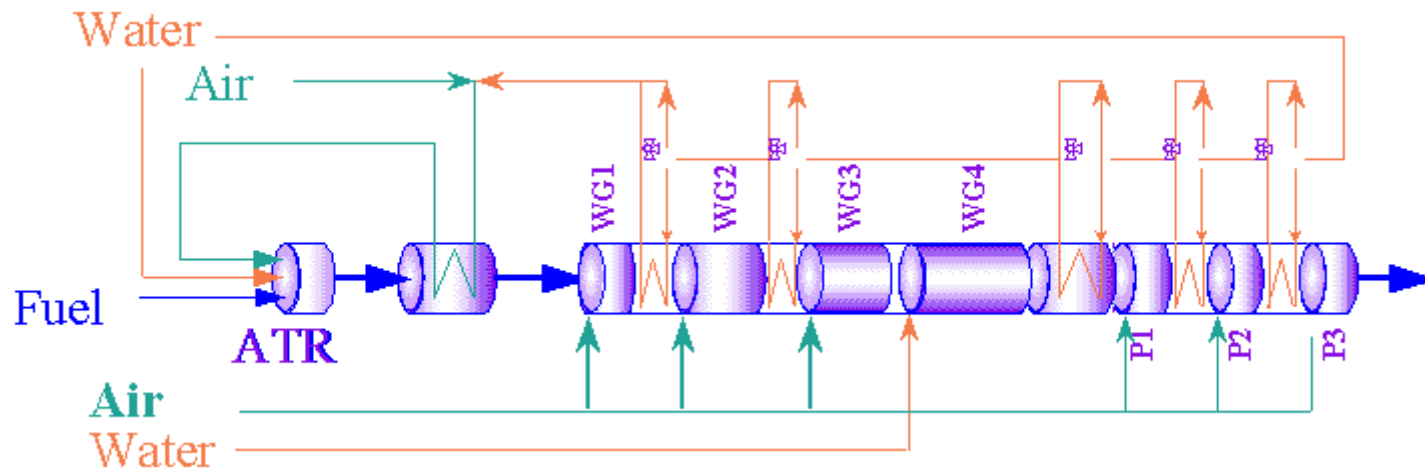
Model predicts 84% efficiency at design point

	ATR	WG1	WG2	WG3	WG4	P1	P2	P3
GHSV, per hr	74K	66K	41K	22K	13K	37K	37K	37K
Catalyst Weight, kg	0.15	0.24 (9%)	0.38 (16%)	0.69 (28%)	1.15 (47%)	0.29	0.29	0.29
Inlet Temperature, °C		375	350	300	280	140	140	100
Exit Temperature, °C	775	440	367	310	287	220	188	113
O/C Ratio (at Inlet)	0.75							
S/C Ratio (at Inlet)	2.1				2.3			
H ₂ at Exit, %-wet	31.8	37.5	39.1	39.9	39.7	38.7	37.7	37.5
CO at Exit, %-wet	9.7	4.0	2.5	1.6	1.0	0.3	0.1	10 ppm
H ₂ O at Exit, %-wet	23.9	18.1	16.6	15.8	16.9	16.9	17.2	17.2

Heat removal stages are arranged to approximate a preferred temperature profile



Start-up: Produce (H_2+CO) in ATR, oxidize downstream to generate heat



- ❖ Bring ATR to temperature in 10 seconds
 - Liquid fuel and water injected into ATR
- ❖ Hydrogen produced in ATR is catalytically oxidized in the shift reactor to generate heat
 - Heat up first three stages only during start-up
- ❖ PrOx catalysts are active at room temperature
 - Sized to handle 4% CO

More than 9-g of gasoline will be needed to heat the catalysts in 60 seconds (10 kWe)

- For start-up, only the catalyst zones need to be at temperature

	ATR	WG1	WG2	WG3	WG4	P1	P2	P3
Catalyst Weight, g	150	235	375	690	1,150	290	290	290
Min. Temperature, °C	500	300	300	250	25	75	75	75
Min. Fuel Required*	9-g (13-mL)							

- Superheated steam and preheated air will be available after heat exchangers are hot

	HE-1	HE-2	HE-3	HE-4	HE-5	HE-6
Ht. Exchanger Weight, g	1100	586	586	943	943	943
Avg. Temperature, °C	570	400	330	225	180	140
Min. Fuel Required [†]	15-g (21-mL)					

- For steady state, catalysts will need to be at design temperature
- Minimum 34-g of gasoline will be needed per start
 - For 50 kWe : 0.07 gals or 1.5 MJ of fuel per start

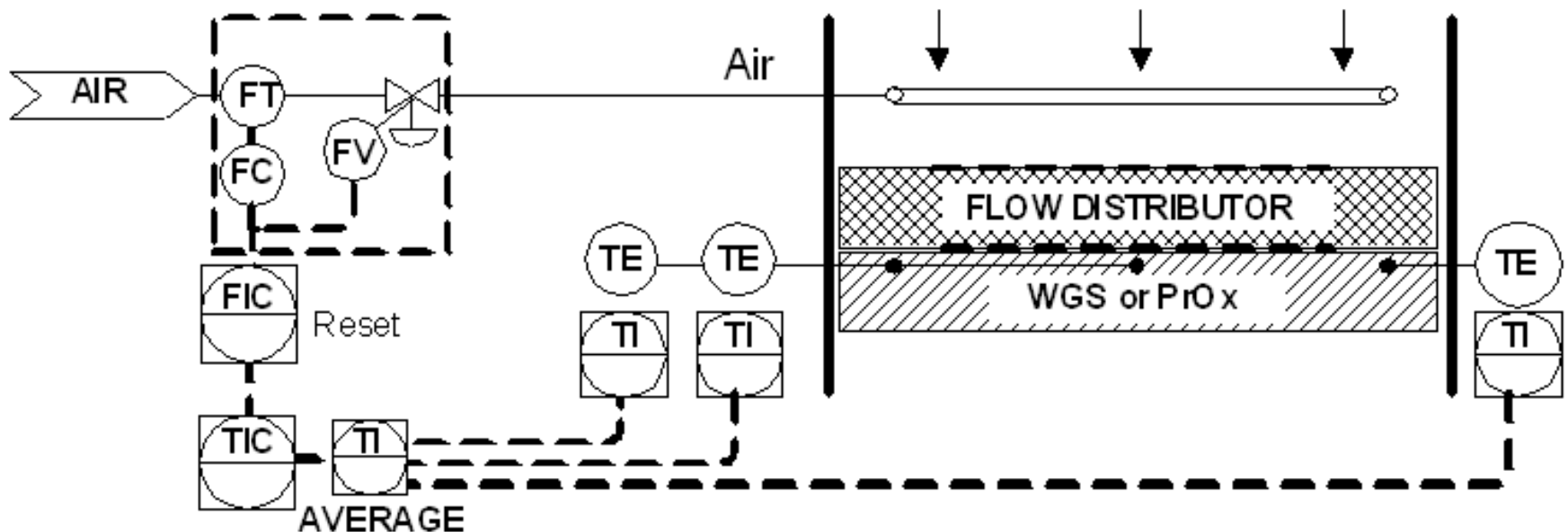
*Fuel Rate at 10 kWe □ 42 g/min

†At 100% heat transfer effectiveness

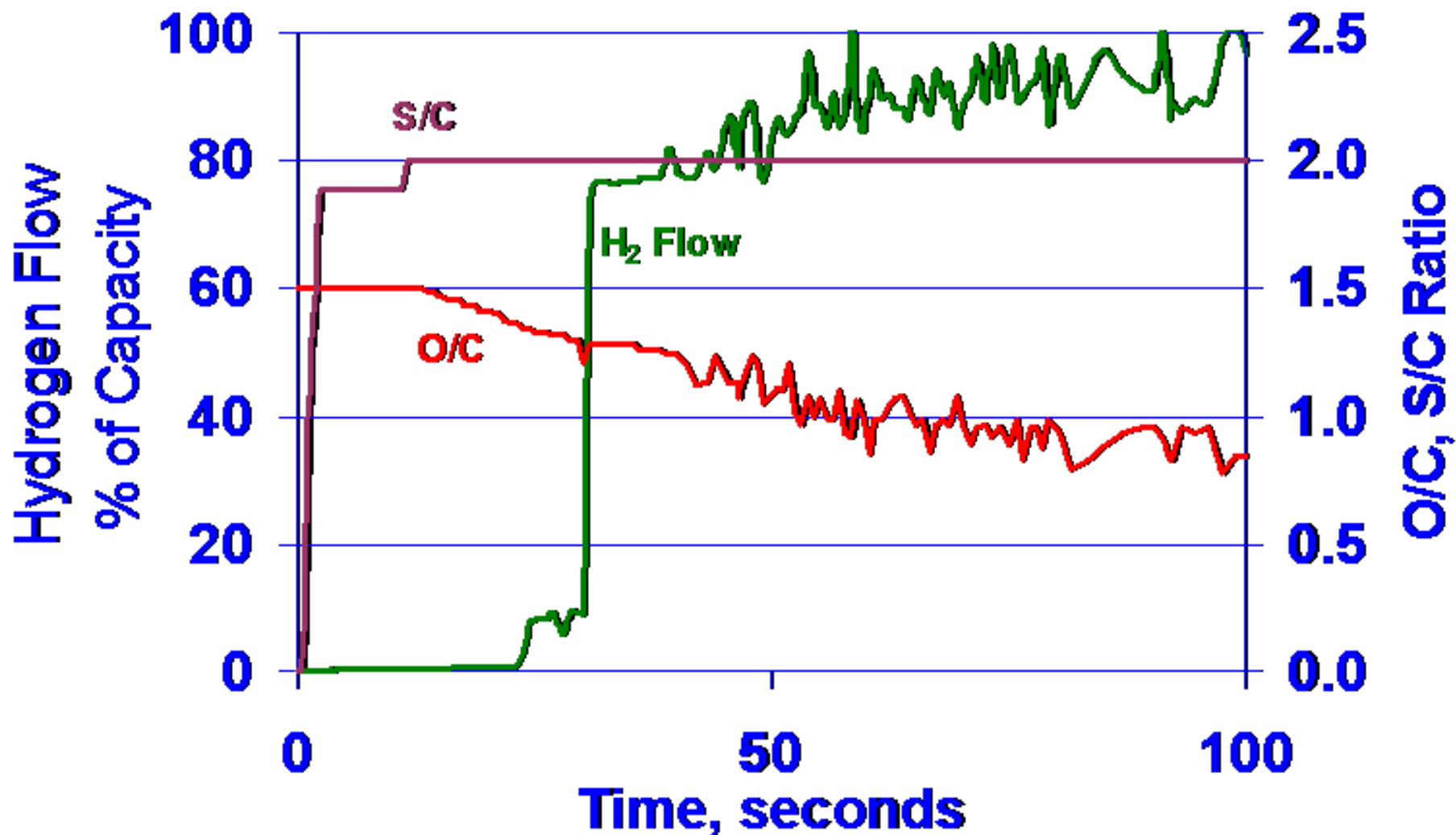
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Start-up performance will rely on timely execution of control algorithm

- Cascade control
 - ❖ Field instruments – MFCs, thermocouples, signal averaging, etc.
 - ❖ Hardware - Opto22, National Instruments, etc.
 - ❖ PC-based software - direct digital control (DDC) - LabView, iFix-Intellution, etc.
- Hardware based control for loops requiring fast response

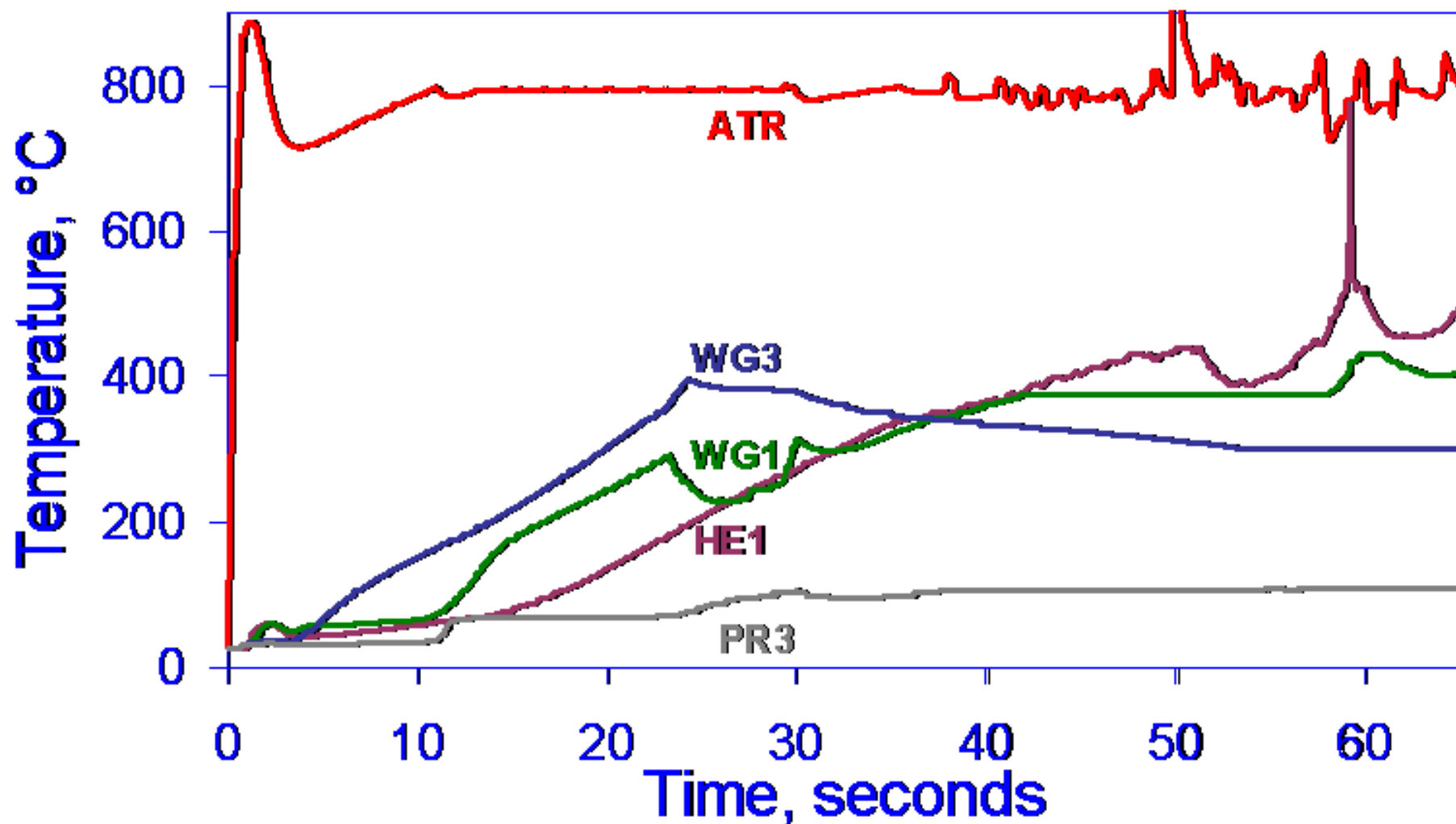


Model: O/C and S/C ratios are adjusted to yield 90% of H_2 capacity in 60s



The critical catalyst zones can be heated quickly

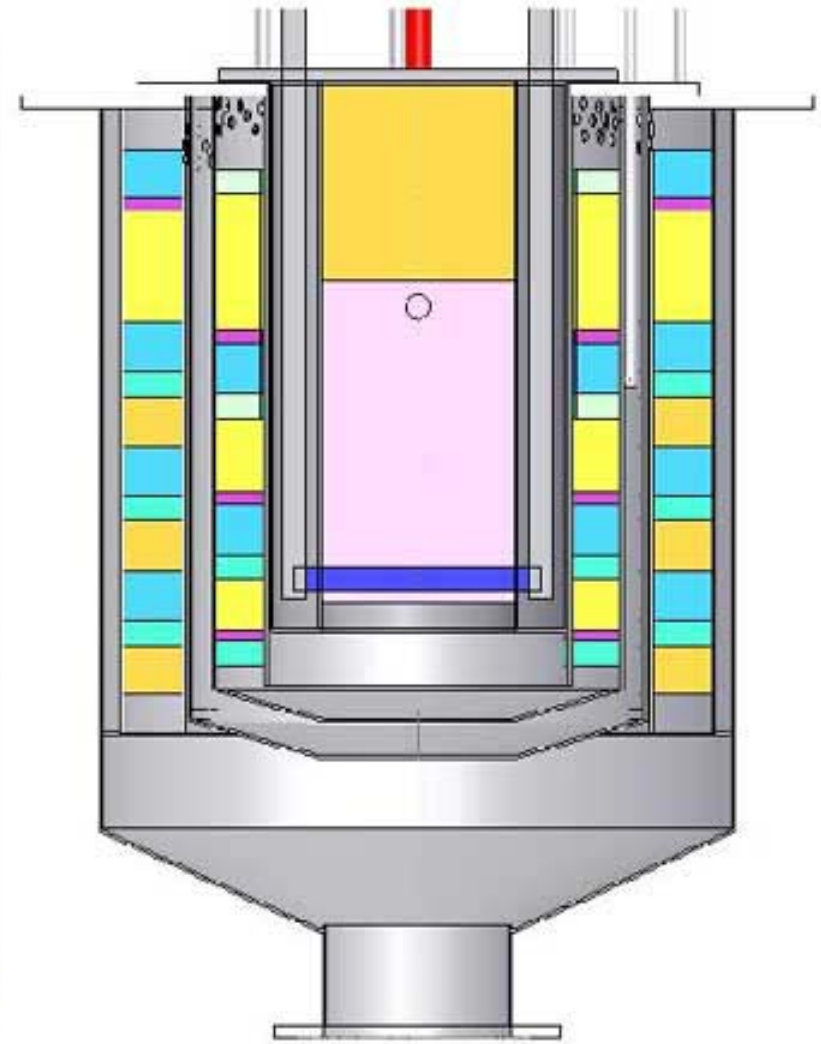
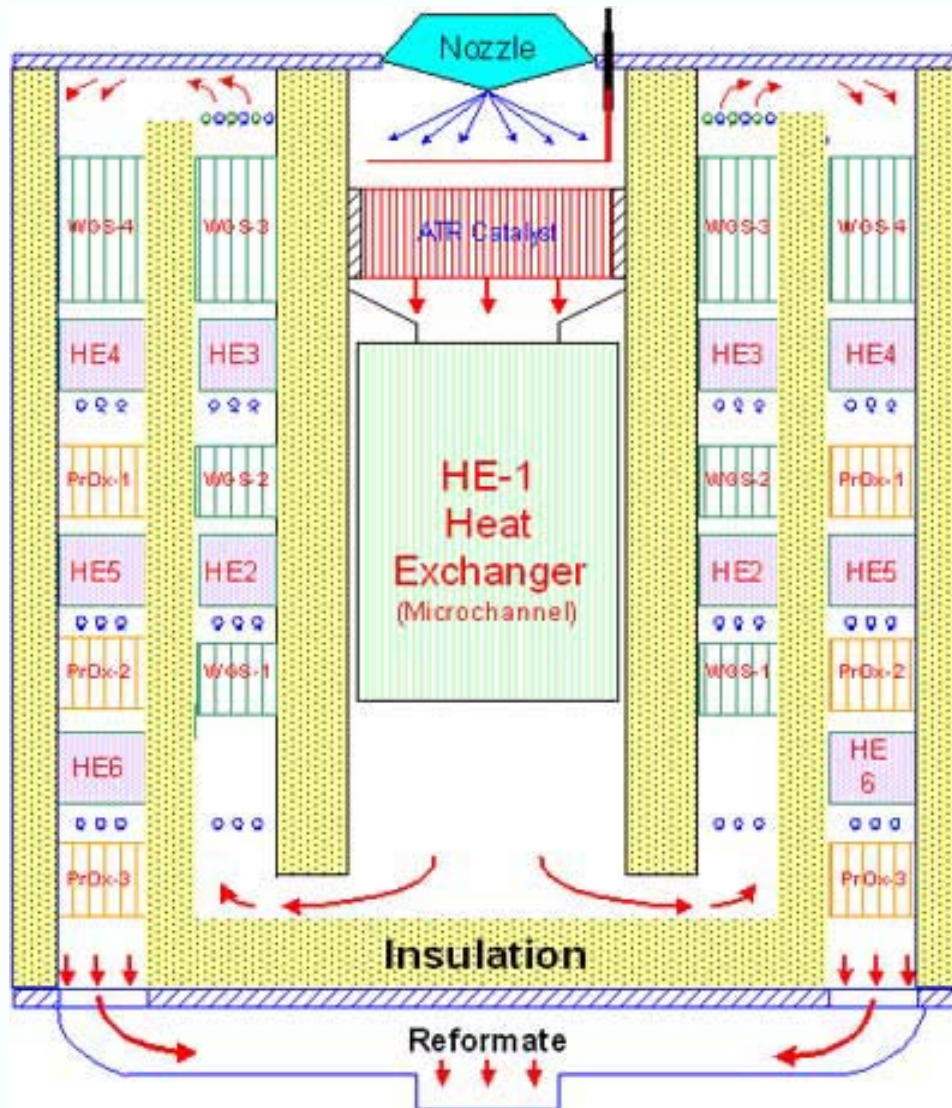
- Catalyst durability will depend on controlling temperature rise



When the fuel processor is better than the sum of its parts

- ❖ Precision Combustion Inc.
 - Microlith™ -based ATR and WGS catalyst assemblies
- ❖ ArvinMeritor
 - Reactor Fabrication and Prototyping
- ❖ Quantum Group Inc.
 - CO sorbent
- ❖ Los Alamos National Laboratory
 - PrOx technology and catalyst assemblies
- ❖ Oak Ridge National Laboratory
 - Carbon Foam heat exchangers for WGS, PrOx cooling
- ❖ Pacific Northwest National Laboratory
 - Microchannel heat exchanger between ATR & WGS-1
- ❖ University contributions
 - Sensors (IIT), Controls (Purdue-Calumet, IIT)
- ❖ Argonne National Laboratory
 - Modeling, system assembly, control, testing, analysis

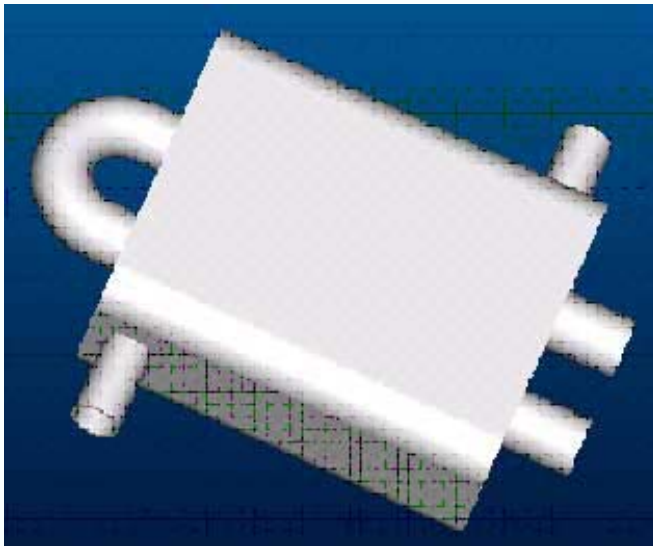
Layout of the Fuel Processor Components



Custom fuel vaporizer and nozzle should enhance reformer performance

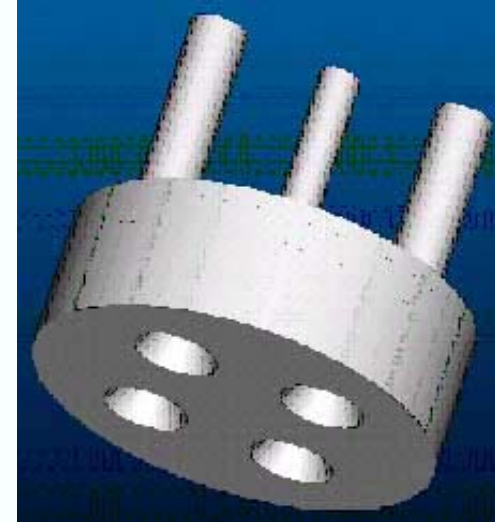
- ❖ Compact vaporizer
- ❖ Heated with gas from spent-gas burner
- ❖ Electrically heated during start-up

L=98 mm; W=48 mm; H=120 mm



- ❖ Nebulize liquids (fuel, water) during start-up
- ❖ Spray vaporized fuel, steam, preheated air during normal operations

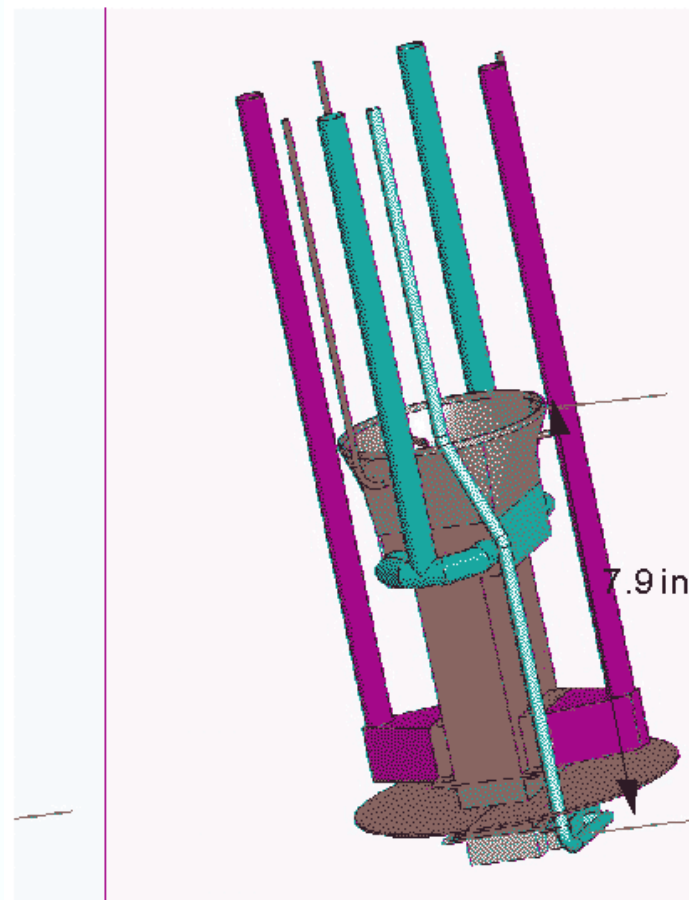
D=70 mm; H=24 mm



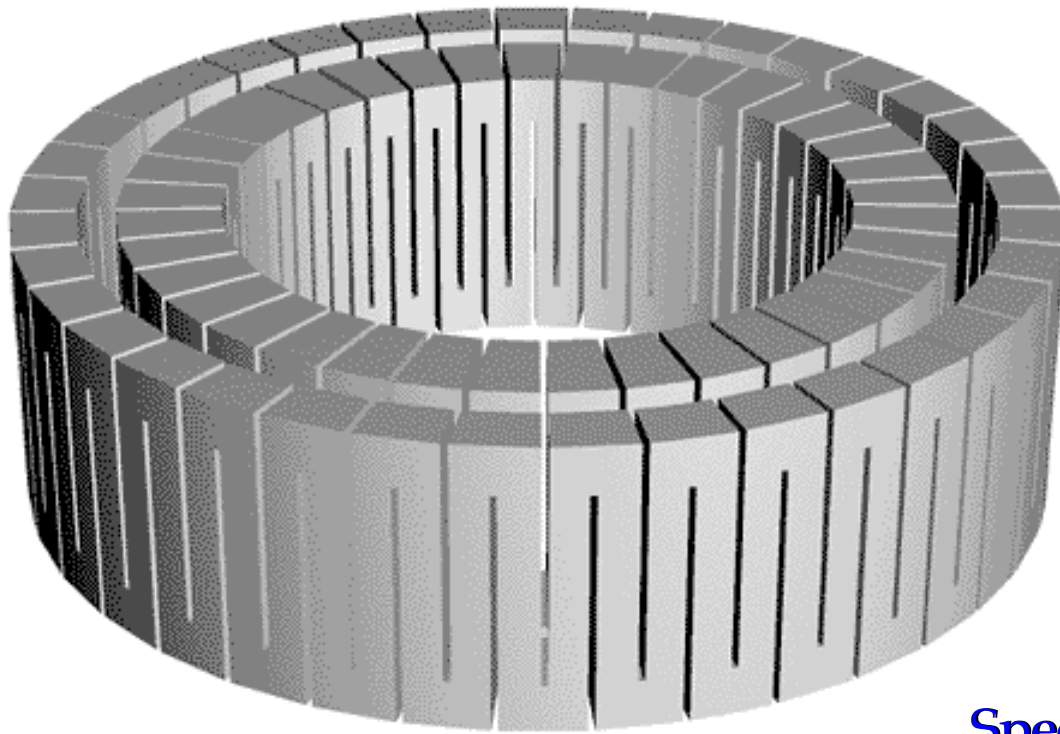
Microchannel Recuperator fits below ATR in the central cylinder

Microchannel Recuperator

- 100°C hot end approach
- 3.6 kW duty
- Approx 1.1 kg
- $\Delta P_{\text{cold}} + \Delta P_{\text{hot}} < 0.4$ psi total
- Uniform outlet temperature



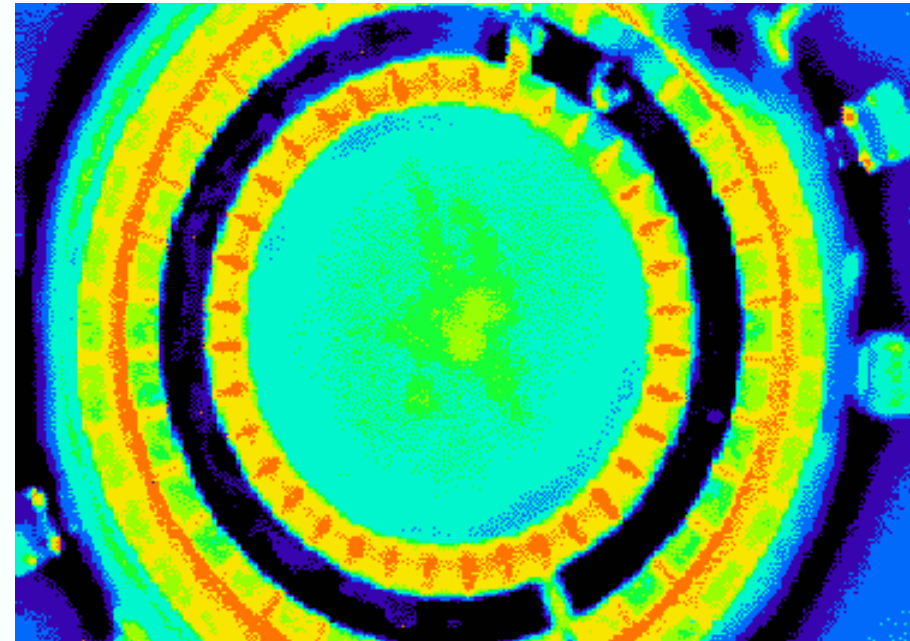
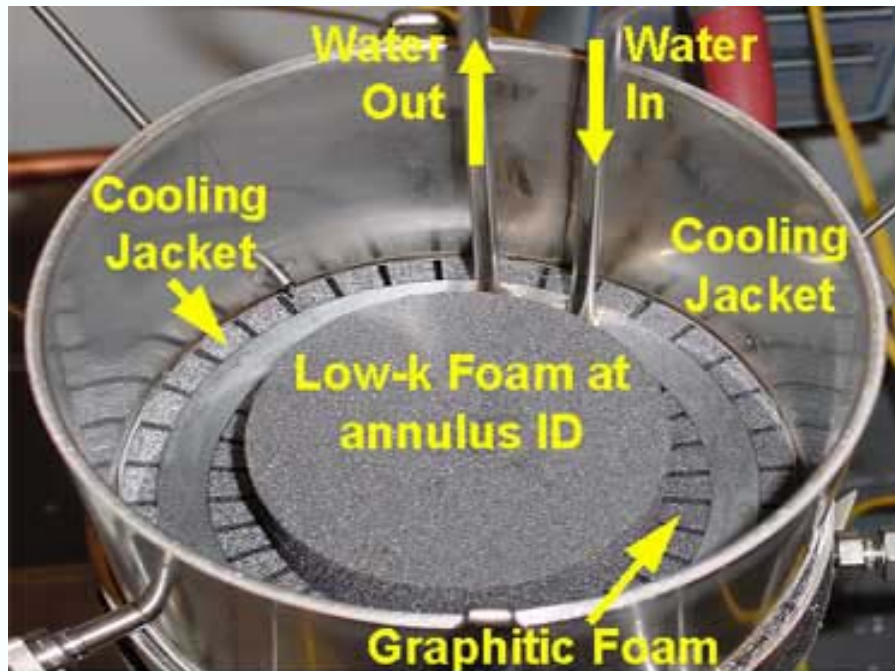
Annular heat exchangers were designed to match heat load and pressure drop constraints



Specifications

- ❖ Hot Gas : Flow = 300 slpm
 $\Delta T > 100^{\circ}\text{C}$ (symmetric)
 $\Delta P < 0.1$ psi
- ❖ Coolant : Water, 2-phase

Tests indicate rapid, symmetric cooling and low pressure drop



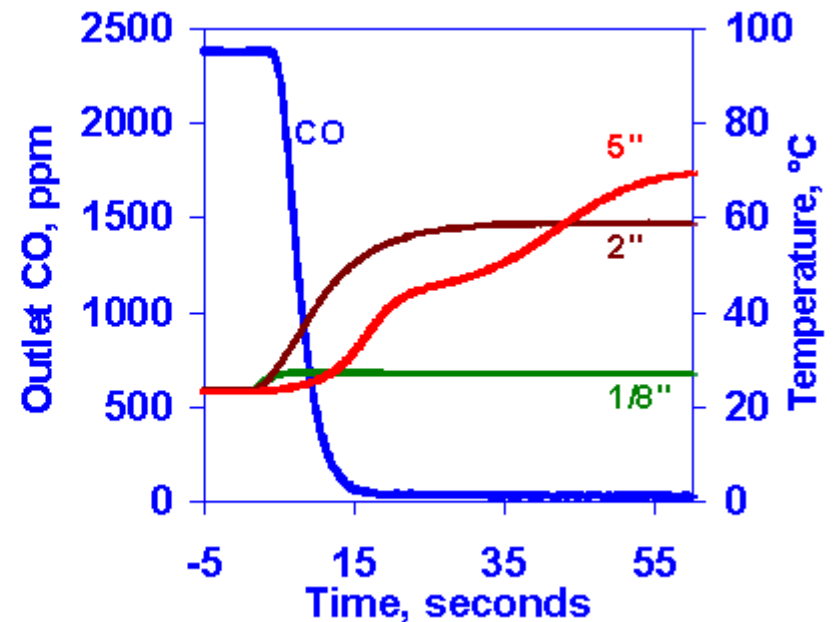
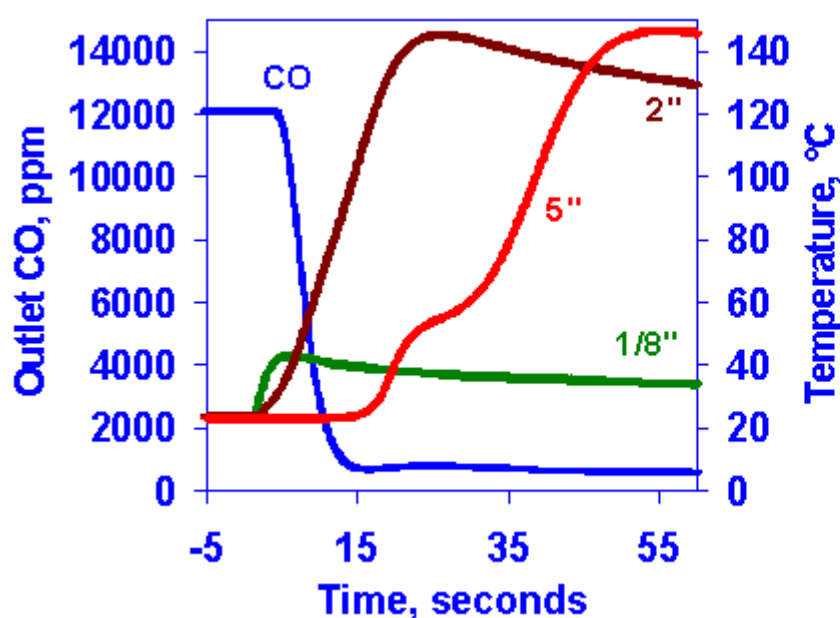
Test Data

- ❖ Hot Gas: Flow = 307 slpm
 $\Delta T \sim 200^{\circ}\text{C}$ (symmetric)
 $\Delta P < 0.04$ psi



PrOx is designed to oxidize up to 4% CO at start-up

- ❖ Defined catalysts and supports with low thermal mass
 - GHSV = 13,000 /hr, Wt. = 0.87 kg
- ❖ Experiments indicate 1.2% CO can be converted in 2-stages
 - 4% CO conversion in 3-stages to be confirmed



Progress and Accomplishments

- ❖ Determined kinetics of ATR, WGS, PrOx catalysts
- ❖ Modeled FP system to define design point
- ❖ P&ID complete
- ❖ Modeled to establish mixing characteristics
- ❖ Reactor design completed
 - DFM in progress
- ❖ Designed nozzle and vaporizer
- ❖ Studying ignition and catalytic oxidation rates of reformat gas
- ❖ PNNL : Designed micro-channel heat exchanger to fit below ATR
- ❖ ORNL : Designed foam heat exchangers for annular geometry
 - Experiments in progress to confirm projections
- ❖ LANL : Verified PrOx activity and response at room temperature

Project Schedule

ID	Task Name	Finish	2003											
			J	F	M	A	M	J	J	A	S	O	N	D
1	Project Duration	Fri 1/30/04												
2	System Definition	Fri 9/27/02												
3	Modeling	Fri 1/30/04												
7	R&D Solutions	Fri 7/18/03												
13	Reactor - Spec to Assembly	Mon 9/15/03												
14	Component Specs	Wed 3/12/03												
17	Receive Components	Thu 7/31/03												
25	Assembly	Mon 9/15/03												
28	FP System Engineering	Fri 6/6/03												
29	Develop Block Flow Diagram	Fri 3/7/03												
30	P&ID	Wed 4/16/03												
35	Bill of Materials	Fri 5/9/03												
40	Long Lead Items	Fri 5/2/03												
43	System Layout	Fri 6/6/03												
48	Control System and EE	Fri 10/24/03												
60	Procurement	Thu 7/3/03												
73	Lab Set-up	Fri 7/25/03												
82	System Fabrication	Thu 10/23/03												
83	Process and Mechanical	Fri 10/10/03												
91	Electrical and Control	Fri 10/10/03												
97	Analytical	Fri 7/25/03												
98	Safety Review	Thu 10/23/03												
101	Testing	Fri 12/19/03												
116	Total System Testing	Fri 1/9/04												
117	Demonstration	Fri 1/30/04												

- Reformate Ignition
- Fuel Vaporizer
- Nozzle evaluation
- Ignition w/ liquid fuel
- ATR Catalyst

Test Plan

Focus on reliable control to execute start-up strategy

- ❖ Confirm ATR start-up and control *Jul.*
 - From manual to automated
- ❖ Add next component and confirm performance *Sep.*
- ❖ Execute start-up strategy in slow mode *Dec.*
- ❖ Accelerate start-up process incrementally *Jan.*
- ❖ Benchmark start-up, steady-state performance *Jan.*
- ❖ Report progress and recommendations to DOE *May*

Can on-board fuel processors meet the start-up target?

- ❖ Time and fuel needed to reach rated efficiency
- ❖ Rate limiting step
- ❖ Failure modes and solution
- ❖ Core R&D needs and priority

Summary

- ❖ A collaborative effort is underway to study fast-start feasibility of on-board fuel processors
- ❖ A laboratory-scale fuel processor has been defined
- ❖ Models predict start-up in 60 seconds is feasible
- ❖ The study contributes to state of fuel processing technology and promotes technology transfer

Contributors

❖ ANL

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- Greg Whyatt
- Larry Pederson